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## DESCRIPTION

WORKED MOLYBDENUM-ALLOY MATERIAL, WHICH IS SUBJECTED TO  
NITRIDING, HAVING HIGH CORROSION RESISTANCE, HIGH STRENGTH,  
5 AND HIGH TOUGHNESS AND METHOD FOR MANUFACTURING THE WORKED  
MOLYBDENUM-ALLOY MATERIAL

## Technical Field

The present invention relates to a worked molybdenum-  
10 alloy material, which is subjected to nitriding, having  
improved strength, toughness, and corrosion resistance as a  
result of a combination treatment of internal nitriding and  
external nitriding, and a method for manufacturing the  
worked molybdenum-alloy material subjected to nitriding.

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## Background Art

Molybdenum (Mo) that has, for example, a high melting  
point (about 2600°C), relatively high mechanical strength  
superior to other metals having high melting points, a low  
20 thermal expansion coefficient, excellent electrical  
conduction and thermal conduction properties, and a high  
corrosion resistance to a melted alkali metal and  
hydrochloric acid, can be applied to, for example,  
electrodes, components for vessels, components for  
25 semiconductors, components for heat-resistant structures,

and materials for nuclear reactors.

A worked material having a worked structure exhibits high toughness due to suppressed crack growth. However, in a material recrystallized by heating (about 1050°C or more), strength at high temperatures is not satisfactory because a crack readily grows to cause embrittlement. Therefore, Mo-Ti(0.5)-Zr(0.08)-C(0.03) (TZM) alloy and Mo-Nb(1.5)-Ti(0.5)-Zr(0.03)-C(0.03) (TZC) alloy have been developed as molybdenum alloys having improved strength at high temperatures.

The inventors found that, in a worked refractory-metal-alloy such as an ultrafine-nitride-containing molybdenum alloy formed by multi-step internal nitriding treatment, high toughness and high strength are achieved by maintaining a worked structure in at least the surface region of the worked material (patent document 1, non-patent documents 1 to 3).

Molybdenum has excellent properties as described above. However, molybdenum has no corrosion resistance against oxidizing acids such as nitric acid and hot concentrated sulfuric acid. Regarding the improvement of the corrosion resistance, the inventors developed a highly corrosion-resistant molybdenum-based composite material having a molybdenum nitride ( $\text{Mo}_2\text{N}$ ) with a thickness of 0.5 to 10  $\mu\text{m}$  produced by nitriding molybdenum and a molybdenum alloy

(patent document 2).

Patent document 1: Japanese Unexamined Patent Application  
Publication No. 2001-73060.

Patent document 2: Japanese Unexamined Patent Application  
5 Publication No. 11-286770.

Non-patent document 1: Masahiro Nagae, Jun Takada, Yoshito  
Takemoto, Yutaka Hiraoka, and Tetsuo Yoshio. J. Japan Inst.  
Metals, 64(2000)747-750.

Non-patent document 2: Masahiro Nagae, Jun Takada, Yoshito  
10 Takemoto, Yutaka Hiraoka, and Tetsuo Yoshio. J. Japan Inst.  
Metals, 64(2000)751-754.

Non-patent document 3: Masahiro Nagae, Jun Takada, Yoshito  
Takemoto, and Yutaka Hiraoka. Materia Japan, 40(2001)666-667.

#### 15 Disclosure of Invention

Only the metal tantalum (Ta) is useful as a material  
for use in very severe corrosive conditions (for example, a  
boiling concentrated sulfuric acid solution). However,  
tantalum has low strength, in particular, its strength is  
20 low at high temperatures; hence, it is inappropriate for an  
apparatus and a structural material which require high  
strength. The above-described highly corrosion-resistant  
molybdenum-based composite material which is developed as an  
alternative to tantalum by the inventors has a disadvantage  
25 in that a base material is recrystallized during the

manufacturing process to cause the embrittlement of the entire material.

Accordingly, it is an object of the present invention to provide an innovative material, which has properties  
5 which cannot be achieved with conventional materials, i.e., having satisfactory high corrosion resistance and high strength in very severe corrosive conditions, for example, a 75% sulfuric acid ( $H_2SO_4$ ) aqueous solution ( $180^\circ C$ ), in addition to high strength at high temperatures and high  
10 toughness at low temperatures, and to provide a method for effectively manufacturing the innovative material.

The inventors found that a worked molybdenum-alloy material having excellent corrosion resistance against oxidizing acids in addition to high strength and high  
15 toughness was effectively and inexpensively produced by subjecting a worked molybdenum material to a combination treatment of internal nitriding and external nitriding.

That is, a worked molybdenum-alloy material, subjected to nitriding, which has high corrosion resistance, high  
20 strength, and high toughness, includes fine nitride particles formed by subjecting a nitride-forming-metal element dissolved to form a solid solution in an untreated worked molybdenum-alloy material to internal nitriding, the fine nitride particles being dispersed inside the worked  
25 molybdenum-alloy material subjected to nitriding; and a

molybdenum nitride layer formed by subjecting a worked structure or a recovered structure at the surface of the untreated worked molybdenum-alloy material to external nitriding, the molybdenum nitride layer being provided at  
5 the surface of the worked molybdenum-alloy material subjected to nitriding.

In the above-described worked molybdenum-alloy material subjected to nitriding, the molybdenum nitride layer at the surface of the worked molybdenum-alloy material subjected to  
10 nitriding is composed of at least any one of  $\delta$ -MoN,  $\gamma$ -Mo<sub>2</sub>N, and  $\beta$ -Mo<sub>2</sub>N.

In the above-described worked molybdenum-alloy material subjected to nitriding, a layer between the molybdenum nitride layer and the matrix in the inside of the worked  
15 molybdenum-alloy material subjected to nitriding has a worked structure or recovered structure.

In the above-described worked molybdenum-alloy material subjected to nitriding, the inside of the worked molybdenum-alloy material subjected to nitriding has a recrystallized  
20 structure.

A method for manufacturing a worked molybdenum-alloy material subjected to nitriding includes the steps of subjecting an untreated worked alloy in which at least any one of titanium, zirconium, hafnium, vanadium, niobium, and  
25 tantalum is dissolved to form a solid solution in a

molybdenum matrix to multi-step internal nitriding treatment including a stepwise increase of the treatment temperature, and then subjecting the worked alloy to external nitriding treatment.

5        In the method for manufacturing a worked molybdenum-alloy material subjected to nitriding, the internal nitriding treatment is performed with a nitrogen gas, and then the external nitriding treatment is performed with an ammonia gas.

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#### Brief Description of the Drawings

Fig. 1 is a schematic cross-sectional view of a worked molybdenum-alloy material subjected to nitriding of the present invention. Fig. 2 is a schematic view showing the structures of a worked material at each step (1) to (3) of the internal nitriding treatment in a manufacturing process of a worked molybdenum-alloy material subjected to nitriding. Fig. 3 is a graph showing the results of a corrosion test of a worked molybdenum-alloy material, which is subjected to nitriding, produced in EXAMPLE 1 and EXAMPLE 2 and also showing the result of a pure molybdenum material in COMPARATIVE EXAMPLE. Fig. 4 shows a photograph (a), which is an alternative to a drawing, of the cross-sectional structure of a worked molybdenum-alloy material subjected to nitriding, and also shows a macro photograph (b), which is

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an alternative to a drawing, after a specimen of a worked molybdenum-alloy material subjected to nitriding was tested by bending. The worked alloy shown in the photographs (a) and (b) are produced in EXAMPLE 2.

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#### Best Mode for Carrying Out the Invention

Fig. 1 is a schematic view showing an example of the cross-sectional structure of a worked molybdenum-alloy material subjected to nitriding of the present invention.

10 The worked molybdenum-alloy material subjected to nitriding shown in Fig. 1 has a triple-layer structure including a layer having nano-size nitride particles 2 dispersed in the surface region of a worked alloy material 1; a molybdenum nitride ( $\text{Mo}_2\text{N}$ ) surface layer 4 produced by subjecting a  
15 worked structure or a recovered structure 3 to external nitriding; and a molybdenum recrystallized layer 5. When a worked material composed of an alloy is relatively thin, a worked structure can be completely maintained through the entire worked material. In this case, a double layer  
20 structure is produced without the molybdenum recrystallized layer 5.

A worked material is produced by processing, for example, rolling a dilute alloy which has a matrix composed of molybdenum and in which at least any one of titanium (Ti),  
25 zirconium (Zr), hafnium (Hf), vanadium (V), niobium (Nb), or

tantalum (Ta) is dissolved to form a solid solution. The term "dilute alloy" means an alloy in which the content of the solute element(s) in a solid solution alloy is about 5 percent by weight or less.

5       A worked molybdenum-alloy material, which is subjected to nitriding, having high corrosion resistance, high strength, and high toughness according to the present invention is manufactured by an internal nitriding treatment including steps (1) to (3) and an external nitriding  
10   treatment (4) described below. Fig. 2 shows schematic views (1) to (3) illustrating the structures of a worked material at each step (1) to (3), respectively, of the internal nitriding treatment including a stepwise increase of the heating temperature.

15       (1) First nitriding step: A worked material is heated in a nitriding atmosphere between a temperature 200°C lower than the lower limit temperature of recrystallization and the upper limit temperature of recrystallization to nitride a nitride-forming-metal element. As a result, a worked  
20   material in which ultrafine nitride particles are dispersed is formed. In this first nitriding step, nitrogen is diffused into a worked dilute-alloy material while maintaining a worked structure X1 in the worked material. As a result, the nitride-forming-metal element that is  
25   dissolved to form a solid solution in a matrix is subjected



to preferential nitriding to form subnano nitride particles, which have diameters of about 1 nm to about 2 nm, in the form of plates, the subnano nitride particles being dispersed in the matrix. The term "preferential nitriding" means a phenomenon in which a nitride-forming-metal element alone is preferentially nitrided but a metal constituting a matrix is not nitrided. A recrystallization temperature is increased due to the pinning effect of the particles precipitated during this nitriding step.

(2) Second nitriding step: The worked alloy produced by the first nitriding step is heated at equal to or more than the lower limit temperature of recrystallization of the worked material in a nitriding atmosphere, thus leading to the grain growth and the stabilization of the ultrafine nitride particles. The grain growth and the stabilization of the precipitated particles induced by this second nitriding step further increase the recrystallization temperature. In nitriding, recrystallization occurs inside a worked material but a worked structure X2 still remains. When a worked material is relatively thin (3 mm or less), a worked structure can be completely maintained through the entire worked material.

(3) Third nitriding step and steps following the third step: The worked material produced by the previous steps is heated in a nitriding atmosphere at equal to or more than

the lower limit temperature of recrystallization of the worked material, thus leading to the grain growth and the stabilization of the nitride particles. An object of the third step and steps following nitriding in the third step  
5 is to further grow and to further stabilize the nitride particles while retaining a worked structure X3. Bar-shaped nitride particles having a thickness of about 10 nm and having a length of about 50 nm are uniformly dispersed in the molybdenum matrix. For example, fourth and fifth  
10 nitriding steps after the third nitriding step can be performed, if necessary.

(4) External nitriding treatment: A molybdenum nitride layer is formed by a strong nitriding treatment. An ammonia gas atmosphere, a nitrogen gas atmosphere, a forming gas  
15 atmosphere (the ratio of hydrogen gas to nitrogen gas is 1:9 to 5:5), and an atmosphere produced by subjecting each gas to plasma discharge, may be used as a nitriding atmosphere. Molybdenum nitride formed is at least any one of  $\delta$ -MoN,  $\gamma$ -Mo<sub>2</sub>N, or  $\beta$ -Mo<sub>2</sub>N. The external nitriding treatment is  
20 performed such that a worked structure or a recovered structure remains between the molybdenum nitride surface layer and the matrix of the inside of the worked material.

Table 1 shows the relationship between the temperature of heating treatment and the thickness of the surface layer  
25 of a Mo-Ti-alloy (Ti content: 0.5 percent by weight). The

layer thickness increases with the increase in heating temperature. It is better to increase the layer thickness in view of corrosion resistance. However, it was found that toughness (bending properties) was reduced with the increase in layer thickness. Therefore, striking a balance between toughness and corrosion resistance requires that the external nitriding treatment (about 3 mm or less of layer thickness) be performed at 900°C or less.

10 (Table 1)

	Pure Mo	Material subjected to internal nitriding up to third step	(Internal nitriding up to third step) + (external nitriding) (2.8 $\mu$ m)
Yield strength	550 MPa	1190 MPa	1280 MPa
Maximum strength	750 MPa	1020 MPa	1870 MPa

A worked molybdenum-alloy material subjected to nitriding of the present invention is useful for, for example, supporting plates for semiconductors, ceramics, and metals; heaters for high-temperature furnaces; components for high-temperature furnaces; structural materials for

chemical equipment and apparatuses used in corrosive atmospheres (including high-temperature incinerators); and materials for reactors with supercritical solutions and/or subcritical solutions. In addition, the worked molybdenum-  
5 alloy material subjected to nitriding is also useful for, for example, acid-resistant vessels and tubes for oxidizing acids such as sulfuric acid and nitric acid; materials for apparatuses used in very severe corrosive conditions (for example, a boiling concentrated sulfuric acid solution);  
10 ultra-high-temperature heaters; injection molds for metals; and injection nozzles for diesel engines.

#### EXAMPLES

##### EXAMPLE 1

A worked Mo-Ti-alloy (Ti content: 1.0 percent by  
15 weight) in the form of a plate having a side of 10 mm and a thickness of 1 mm was subjected to internal nitriding up to the fourth step at predetermined heating temperatures in a nitrogen gas flow (1 atm). The profile of the heating temperature was set as follows: 900°C → 950°C → 1200°C →  
20 1500°C.

By this multi-step nitriding treatment, the surface region of the worked material (up to about 200 μm in depth from the surface) maintained a worked structure or a recovered structure (the inside of the worked material  
25 consisted of a recrystallized structure). In addition, fine

titanium nitride particles were precipitated and dispersed in the surface region. Subsequently, external nitriding treatment was performed at 1000°C for 4 hours in an ammonia (NH<sub>3</sub>) gas flow (1 atm) to form a molybdenum nitride (for  
5 example,  $\gamma$ -Mo<sub>2</sub>N) layer having a thickness of 14.0  $\mu$ m at the surface of the worked material.

This worked material had a triple layer structure as follows: The surface of the worked material was composed of a molybdenum nitride layer. The inside of the molybdenum  
10 nitride layer was composed of a nitride layer of an element which is dissolved to form a solid solution in a molybdenum matrix of a worked structure or a recovered structure in which fine titanium nitride (TiN) particles are precipitated and dispersed. The inside of the nitride layer is composed  
15 of a molybdenum-alloy layer having a structure with isometric and coarse recrystallized grain.

Fig. 3 shows the results of a corrosion test in a boiling 75% concentrated sulfuric acid solution at 185°C in order to evaluate corrosion resistance in severe corrosive  
20 conditions. Fig. 3 also shows the results of pure molybdenum as a reference. As shown in Fig. 3, the pure molybdenum was heavily corroded and exhibited a high corrosion rate of 8 mm/year, while the worked material (EXAMPLE 1) of the present invention was hardly corroded and  
25 exhibited a corrosion rate of 0.076 mm/year. That is, it

was found that the worked material of the present invention exhibited substantially complete corrosion resistance ((corrosion rate)<0.05 mm/year).

#### EXAMPLE 2

5       A worked Mo-Ti-alloy material (Ti content: 0.5 percent by weight) was subjected to internal nitriding up to the third step at predetermined heating temperatures in a nitrogen gas flow (1 atm). The profile of the heating temperature was set as follows: 900°C → 1200°C → 1500°C.

10   The resulting Mo alloy subjected to the internal nitriding up to the third step was further heated (external nitriding treatment) at 900°C for 4 hours in an ammonia gas flow (1 atm) to uniformly form a molybdenum nitride ( $\delta$ -MoN,  $\gamma$ -Mo<sub>2</sub>N) layer at the surface of the worked material. The internal

15   nitrided layer composed of a worked structure or a recovered structure, in which fine titanium nitride particles were precipitated and dispersed by the multi-step nitriding treatment, had a thickness of 310  $\mu$ m. The external nitrided layer composed of molybdenum nitride had a thickness of 2.8

20    $\mu$ m. An X-ray diffraction pattern showed that  $\delta$ -MoN and  $\gamma$ -Mo<sub>2</sub>N were formed at the external nitrided layer.

Fig. 3 shows the results of a corrosion test in a boiling 75% concentrated sulfuric acid solution at 185°C. The worked material of EXAMPLE 2 was hardly corroded and

25   exhibited a corrosion rate of 0.046 mm/year. That is, the

worked material exhibited complete corrosion resistance  
((corrosion rate)<0.05 mm/year).

Table 2 shows the bending strength at room temperature  
(yield strength and maximum strength) of a worked material  
5 subjected to internal nitriding up to the third step (900°C  
→ 1200°C → 1500°C) and a worked material subjected to  
external nitriding treatment (at 900°C for 4 hours) after  
internal nitriding up to the third step. Fig. 4 shows a  
photograph (a) of the cross-sectional structure and a macro  
10 photograph (b) of a specimen subjected to the bending test.

(Table 2)

1100°C	1000°C	940°C	900°C	850°C	800°C
4 h	4 h	4 h	4 h	4 h	4 h
30 μm	14.0 μm	4.7 μm	2.8 μm	1.7 μm	1.1 μm

As shown in Table 2, it was found that both yield  
15 strength and maximum strength of the worked material (having  
a molybdenum nitride layer thickness of about 2.8 μm)  
subjected to external nitriding treatment at 900°C for 4  
hours in EXAMPLE 2 represented high stress values at the  
same level as those of the material (highly strengthened and  
20 highly toughened) subjected to only internal nitriding up to  
the third step.

That is, it was proved that a worked molybdenum-alloy material subjected to nitriding of the present invention had very high strength in addition to high corrosion resistance.

## 5 Industrial Applicability

The present invention provides a worked molybdenum-alloy material, which is subjected to nitriding, having high strength and high toughness in addition to high corrosion resistance against oxidizing acids and thus can be used in  
10 the most extreme corrosive conditions. The worked molybdenum-alloy material is effectively and inexpensively produced by only nitriding. The worked molybdenum-alloy material subjected to nitriding contributes to enabling the practical use of molybdenum materials in various  
15 applications such as materials for apparatuses used in very severe corrosive conditions (for example, a boiling concentrated sulfuric acid solution), ultra-high-temperature heaters, injection molds for metals, and injection nozzles for diesel engines, as well as various applications of  
20 conventional molybdenum or molybdenum alloys.